

# Eliminating Particle-Related Artifacts in the Real-Time Measurement of Mercury in Flue Gases

# Interim Progress Report, Phase II

#### Grant Number DE-FG02-99ER86087

Submitted to: Dr. Peter Botros

Department of Energy

National Energy Technology Laboratory

P. O. Box 10940

Pittsburgh, PA 15236-0940

Prepared by: Dr. Daryl L. Roberts

**MSP** Corporation

5910 Rice Creek Parkway, Suite 300

Shoreview, MN 55126

651-287-8100

Date: December 19, 2003

These STTR data are furnished with STTR rights under Grant Number DE-FG02-99ER86087. For a period of four years after acceptance of all items to be delivered under this grant, the Government agrees to use these data for Government purposes only, and they shall not be disclosed outside the Government (including disclosure for procurement purposes) during such period without permission of the grantee, except that, subject to the foregoing use and disclosure prohibitions, such data may be disclosed for use by support contractors. After the aforesaid four-year period, the Government has a royalty-free license to use, and to authorize others to use on its behalf, these data for Government purposes, but is relieved of all disclosure prohibitions and assumes no liability for unauthorized use of these data by third parties. This Notice shall be affixed to any reproductions of these data in whole or in part.

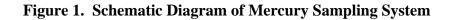
# INTRODUCTION

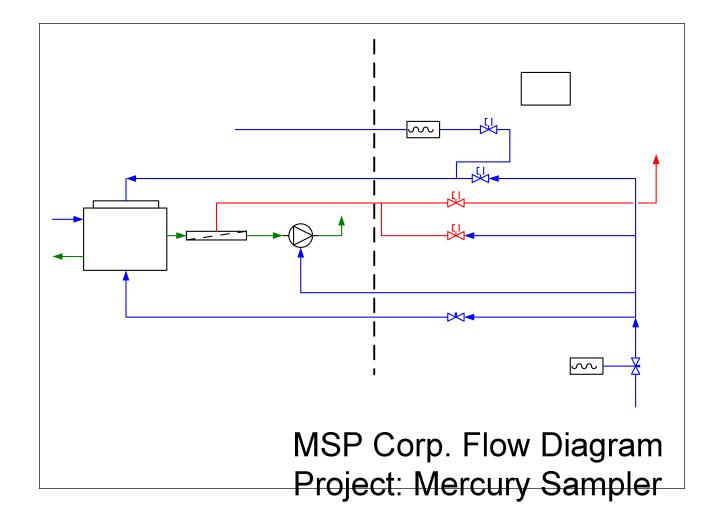
Mercury is one of the 189 trace chemicals listed in the 1990 Clean Air Act Amendments (CAAAs), because of its high volatility, toxicity, and bioaccumlative properties in the food chain, it is environmentally significant. The forms of mercury typically reported in mercury measurement from coal-fired boilers are particulate-bound (Hg<sub>p</sub>), elemental (Hg<sup>0</sup>), and oxidized (Hg<sup>2+</sup>) mercury. It has been found that the chemical form of mercury emissions appears to determine the effectiveness of control strategies and the deposition rate of mercury because of the markedly different chemical and physical properties of the different mercury forms.

MSP has developed this sampler to eliminate the particle-related artifacts commonly found in the measurement of mercury in flue gases. This sampler accumulates no particulate matter but rather disengages the particles from the mercury sample gas via virtual impaction, a technique based on inertial separation of particles as the sample gas flows through carefully designed nozzles. The small fraction of particles smaller than the cutpoint of the virtual impactor remaining in the sample line is also removed by a high-efficiency filter with a stainless steel porous metal filter element. Therefore, the sample provided to the mercury analyzer is completely particle-free (no additional filtration is required to protect the mercury analyzer)

Figure 1 shows the schematic diagram of sampler. The opposing-jet virtual impactor (OJ-VI) is especially energy efficient and minimizes internal deposition of particles in the sampler (Liu et al., 2003, Romay, et al, 2002, Marple and Liu, 1987). The surrounding flue gas is drawn into the sampler using an ejector pump. The flue gas and the particles in the flue gas accelerate as they are drawn through the first set of nozzles. Upon exiting the nozzles, the flow encounters another set of nozzles called receiving tubes. A compressed air jet ejector draws a small portion of the flow into the receiving tubes. A near-stagnation flow condition takes place at the inlet to the receiving tubes. However, most of the particles have sufficient inertia to proceed into the receiving tubes and exit the sampler in the "minor" flow. The rest of the flow, now largely free of particulate matter, constitutes the "major" flow stream. This stream is now suitable for passing through a cross-flow metal filter before it is introduced to a mercury analyzer or any other analysis equipment.

The sampling system shown in **Figure 1** also provides the ability to clean the internal surfaces of the virtual impactor and the cross-flow filter by back-pulsing clean compressed air. A solid-state timer allows the user to switch between the sampling and the cleaning modes on a pre-programmed schedule. The timer also takes care of controlling the opening and closing of several valves for the back-pulse cleaning without having to remove the sampling probe from the stack. Back-pulsing occurs during a small fraction of the time (less than 1%), allowing the user to have continuous measurement of the mercury concentration in the stack gas.





# DESIGN OF THE MERCURY SAMPLING SYSTEM

The design of the Mercury Sampling System can be divided in three basic subsystems:

- 1. The virtual impactor
- 2. The probe assembly
- 3. The control enclosure

# The Virtual Impactor

The first prototype of the virtual impactor was a two-stage design (Liu et al., 2003) that had a proprietary design to remove particles larger than 0.5 µm by two virtual impactor stages in series. A detailed description of this virtual impactor can be found in references 1 and 4. This design worked well, but it had some disadvantages: (1) the two-stage design was complex (too many machined parts and O-rings), (2) the second stage had a large pressure drop (about 80 in wg), and (3) the virtual impactor was too big to be used in a 4" sampling port.

The second prototype of the virtual impactor is the one described in this report. The improved virtual impactor has a single stage with a 1  $\mu$ m cutpoint in an opposed jet configuration. The single stage virtual impactor has a pressure drop of less than 10 inches of water. The new hexagonal design is smaller in size, lighter and has fewer machined parts compared to the first prototype. It has four machined parts and two Orings. The approximate size of the VI is 2.7 inches in length and it is machined from a nominal 2 inch hexagonal bar.

The second prototype of the virtual impactor consists of a machined main body with two end caps, as shown in **Figure 2**. The main body has machined receiving tubes aligned with the two inlet nozzles machined on the end caps. The nozzles and receiving tubes have been sized to achieve a nominal 1  $\mu$ m cutpoint for the inertial separation of the sampled particles. **Table 1** shows the design flow rates and the calculated cutpoint of the virtual impactor.

**Table 1 Virtual Impactor Design Parameters** 

Parameter	Value
Total Flow (L/min)	15.00
Minor/Total (%)	25
Minor Flow (L/min)	3.75
Major Flow (L/min)	11.25
$(St_{50})^{1/2}$	0.45
D <sub>p,50</sub> (μm)	0.94
Slip Correction Factor	1.18
Number of nozzles	2
W (cm)	0.172
ΔP (in wg)	10.67
Reynolds Number	6034



**Figure 2 - Single Stage Virtual Impactor** 

The virtual impactor has four ports: (1) the sample port (S) for the major flow of the VI (2) the ejector port (E) to supply compressed air to drive the internal ejector pump that suctions the minor flow with the large particles (3) the ejector exhaust port (which goes back to the stack) and (4) the cleaning/pressure sensing port (C) to monitor the pressure drop during sampling and to inject clean compressed air during a cleaning cycle. **Figure 3** - **Virtual Impactor and Ports** shows the virtual impactor with the three main ports required to operate the sampler.



Figure 3 - Virtual Impactor and Ports

# The Probe Assembly

The probe assembly shown in **Figure 4** can be inserted into the stack using the ¼" OD stainless steel rigid lines required to operate the virtual impactor. A cross-flow filter has been attached to the sample port of the VI. The rigid lines are attached to a standard sampling port flange using bulkhead fittings. The probe assembly is approximately 4 ft in length. The heated sampling line is a PTFE ¼" OD flexible tube wrapped by a heated jacket that maintains the line at a temperature of 350 F using a thermocouple and a heater controller.

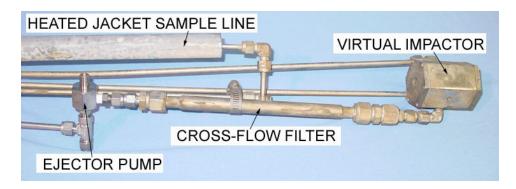


Figure 4 – Sampling Probe Assembly

The cross-flow filter is a porous ( $10 \mu m$ ) stainless steel tubular element. **Figure 5** shows a cross section of the filter. The filtered gas sample flows radially through the porous structure of the filter, while the major flow of the VI flows axially through the center of the filter element. By keeping an axial velocity between 70 and 100 fps this filter configuration significantly reduces the accumulation of particulate matter on the filter element. The cross-flow filter is also back-pulsed during the cleaning cycle. This sampling probe configuration increases the time that the system can run between back-pulse cleaning cycles and eliminates the need to remove the sampling probe from the stack for maintenance. This is highly desirable in continuous emission monitoring (CEM) of stack gases.

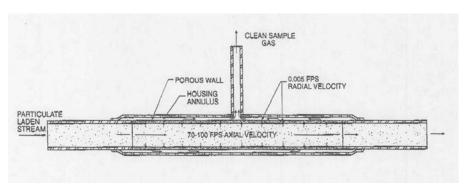


Figure 5 – Mott Cross-Flow Filter Diagram

## **The Control Enclosure**

The control enclosure is a NEMA 4 fiberglass enclosure used to house all the components required to run the stack sampler in its two modes of operation. These components are listed in **Table 2.** *Main Control Enclosure Components* with a short description of their function. **Figure 6** shows the front of the enclosure and **Figure 7** shows the inside of the control enclosure. The front door of the enclosure has the differential pressure gage and the pressure regulator to adjust the compressed air flow for the ejector pump in the VI. The main power switch and the programmable timer are also located on the front panel. To the right of the control box is a pressure regulator and a pressure gage to adjust the input compressed air pressure to the system (45 to 60 psig). All the solenoid valves and the power supply are mounted inside the enclosure. One pneumatically actuated ball valve for the sample line is mounted outside of the enclosure because it needs to be heated.

**Table 2. Main Control Enclosure Components** 

Component	Description	
Power Supply, 100W	Converts 120 VAC to 24VDC for operation of the solenoid valves and timer	
Programmable Timer	Allows to program the sampling and cleaning cycles	
Differential Pressure Gage	Monitors the pressure drop (and flow rate) across the VI	
Pressure Gage	Measures compressed air inlet pressure	
Pressure Regulator 1	Controls compressed air inlet pressure	
Pressure Regulator 2	Adjusts VI ejector for controlling VI inlet flow	
Ball valve 1 (normally open)	Protects the gas analyzer during the cleaning cycle	
Ball valve 2 (normally closed)	Opens during cleaning to backpulse the cross- flow filter	
Solenoid valve 1 (normally closed)	Opens during cleaning to backpulse the VI	
Solenoid valve 2 (normally open)	Closes during cleaning to protect the differential pressure gage	



Figure 6 – Font Door Panel of Control Enclosure



Figure 7 – Rear Panel of Control Enclosure

# FIELD TESTING OF THE MERCURY SAMPLING SYSTEM

#### Introduction

Particulate matter can greatly affect the ratio of the three mercury species normally present in flue gas. It can adsorb mercury or change the species of mercury. Therefore it is very important to develop methods that can help to eliminate the effects of particulate matter when a continuous mercury monitor (CMM) is designed. A novel particulate sampler developed by MSP Corporation has been tested at the bench-scale level to determine how effective it is in eliminating the effects of particulate matter on mercury speciation (Roberts et al., 2001). The results of the bench-scale tests indicate the virtual impactor (VI) system does provide a reasonably low particulate stream with less particulate-mercury interactions than a filter. However, the interaction between particulate matter and mercury may be different in a full-scale system than that encountered in a bench-scale system. Therefore, in June 2002, the MSP sampling system was tested at the Sammis Power Plant and was compared to other sampling systems. Upon completion of this testing MSP corporation made several improvements and tested the system at the Gavin Power Plant. This report addresses the most recent testing conducted at the Gavin Power Plant.

# **Objectives of the Field Testing Program**

The overall goal of the field testing program is to evaluate several particulate collection devices to determine their ability to remove particulate matter from the sample gas stream before it reaches a backup filter. The specific goal of the Gavin Power Plant testing was to compare the MSP sampling system to a Baldwin sampling system. A primary concern in this testing included both total and elemental mercury concentrations.

#### **Description Of The Power Plant**

The evaluation of the MSP sampling system was done at the Gavin Power Plant in Cheshire, Ohio located near Galipolis, Ohio, which is near the Ohio-West Virginia border. The Gavin Plant fires a high-sulfur Ohio bituminous coal and employs SCR followed by an electrostatic precipitator (ESP) and a wet scrubber. Flue gas testing was conducted on Unit 2 with the SCR unit operating normally for the first stage of testing. Approximately 2 days from the end of the test period, the SCR was bypassed, and continuous mercury monitor (CMM) data were collected without the influence of SCR technology. Information about the configuration of the two units is found below:

- Fuel type: Ohio bituminous coal
- Boiler capacity: 1360 MW gross; 1285 MW net
- Boiler type: wall-fired pulverized coal
- NO<sub>x</sub> control: low-NO<sub>x</sub> burners and SCR

Particulate control: ESP

• SO<sub>2</sub> control: wet scrubber

# **Particle Separation Devices**

The two sampling devices tested are described below:

- 1. Single-stage virtual impactor with a cross-flow filter (MSP sampling system) continuously removes particulate from the sample gas stream intermittently cleaned by back-pulsing.
- 2. Baldwin Environmental Inc. (BEI) Inertial Filtration (IF) barrier filter.

The MSP sampling system provided a gas sample as follows. A sampling probe consisting of the single-stage virtual impactor and a cross-flow filter were located inside the stack. The large particles (> 1  $\mu$ m) were removed by the VI minor flow and ejected back to the stack. The major flow containing the remaining small particles entered a cross-flow filter. Only the flow needed by the mercury analyzer was filtered through the porous metal media. The remaining major flow flowed through the center of the porous metal element. The sample flow then flowed up a heated line to a flange connection at the sampling port. At this point, the particle free flue gas would enter an EERC heated umbilical line going to a heated backup quartz thimble filter and then to the conversion unit upstream of the mercury analyzer.

The Baldwin flow path starts by the sample entering a heated probe. Then, the sample is pulled by an eductor through a large continuously cleaned filter, all located inside a heated hot box outside the port. The flow then goes to a heated backup quartz thimble filter and to a pump all inside the same hot box. The final leg is to a heated umbilical leading to the conversion unit upstream of the mercury analyzer.

# Sampling Approach And Locations

Using the two sampling devices mentioned above, samples were taken at the ESP inlet on Unit 2 side by side in the two middle ports. The OH samples were taken in the same port as the MSP system. The intent was to evaluate each device as it ran in continuous operation. During this testing, one CMM was used in conjunction with a switching box to continuously monitor elemental mercury or total gas-phase mercury. An absolute filter was used downstream of each filtration device. Several ESP inlet OH mercury speciation samples were taken for comparison purposes during the testing. The OH samples were collected using a standard in stack quartz thimble filter assembly. A total of 3 OH samples were taken at the ESP inlet location.

The overall testing schedule included setup of the CMMs and other equipment from September 26th through September 28th and testing from September 29th through October 5th. The Baldwin filter assembly was evaluated first (on September 26th) to establish a baseline for comparison. Following this each probe was alternated back and forth every few hours. However, there were problems operating the CMMs and tre sasmpling systems during each of the tests, and generally each device was tested in approximately two-hour time intervals. It should be noted that this power station fires a high sulfur coal and therefore substantial SO<sub>3</sub> is produced. This resulted in plugging of the EERC conversion equipment and downtime for the CMM's.

#### **Results And Discussion**

## Field modifications to the MSP sampling probe

Before proper continuous testing could commence on the MSP system the probe was partially reconfigured for use with the EERC conversion system.

For a standard PSA conversion unit, a pump is generally required to draw the sample. The MSP system did not provide this pump, so a pump in a hot box was used during these tests. A heated umbilical line was run from the conversion unit to the heated pump. A second heated line was run from the inlet of the pump to the MSP sampling probe.

During the initial tests on September 29 it was apparent that the MSP sampling line was condensing some water. The flue gas must be kept above dew point temperature from the inlet of the MSP to the CMM conversion unit. As water condenses in the lines, mercury will collect in the water. If the water droplet then evaporates, all the mercury contained in the droplet will be released, resulting in a spike of mercury measured on the CMM. Also the water droplet can potentially be lost back into the duct or to a low point where moisture can collect resulting in low mercury readings. After looking at the sampling probe inside the stack, it was found that the first foot below the sampling port was colder than the rest of the sampling line due to a stagnant section on upper section of the sampling port. To fix this a film heater controlled by a thermocouple was added to the whole length of the sample line below the sampling port. A solenoid valve in the sample line had also to be bypassed as it was not possible to heat this valve to 350 F. Bypassing this valve did not allow to have periodic back-pulse cleanings on the MSP sampling system.

#### **Mercury Results**

Because fly ash removal had previously been evaluated the primary emphasis of this field tests was to measure mercury speciation and comparing the MSP and Baldwin sampling systems. Upon visual inspection of the backup filters the MSP and Baldwin systems appeared to perform similarly removing particulate matter. Also from the

particulate analysis shown in **Table 4** it should be noted that at the Gavin plant there was no mercury in the particulate and therefore the observed results may change at a plant with higher mercury numbers in the particulate or a with more reactive ash.

Interpreting the mercury results (shown in Figures 8 to 11) is difficult because there is no exact reference method that can be used for comparison, plus there were several operational problems during most of these tests, both in the sampling systems and in the EERC conversion system for the mercury analyzer. Therefore, it was necessary to make inferences about the measurements. This was done by comparing the results of the Baldwin, MSP VI, and OH to each other. However, the OH measurements were taken the week before so they were only used for reference purposes. ESP inlet CMM data can be seen in Figures 8 to 11, with averages of the data for each day which the Baldwin or MSP systems ran in **Table 3**. The OH method data collected over the testing at the ESP inlet are shown in **Table 4**.

Figure 8 (09/30/03) shows the effect of the sampling line particle plugging (specifically the elbow connecting the backpulse flow from the filter to the virtual impactor), with a continuous drop in the total mercury concentration. Figure 9 (10/01/03) shows good total mercury measurements with the MSP system running normally. For this day both the total and elemental mercury concentrations measured by both systems are comparable, but somewhat lower values for the MSP system. Figure 10 (10/02/03) shows again the effect of line plugging with mercury concentrations dropping gradually 8 to 2  $\mu$ g/m³. Figure 11 (10/03/03) shows again comparable total mercury measurements with both sampling systems, but in this run the elemental mercury concentrations were consistently higher with the MSP sampling system.

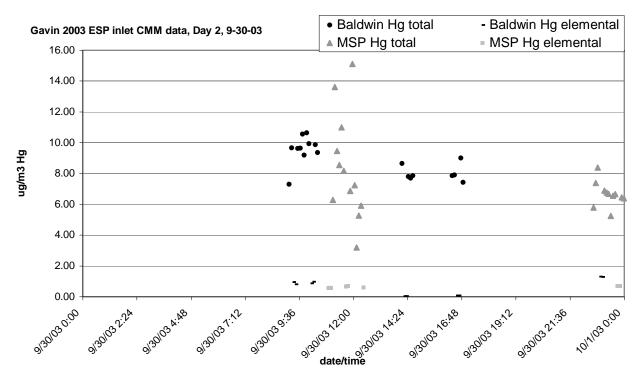


Figure 8: 09/30/03 data at ESP inlet; MSP unit shows effects of particle plugging.

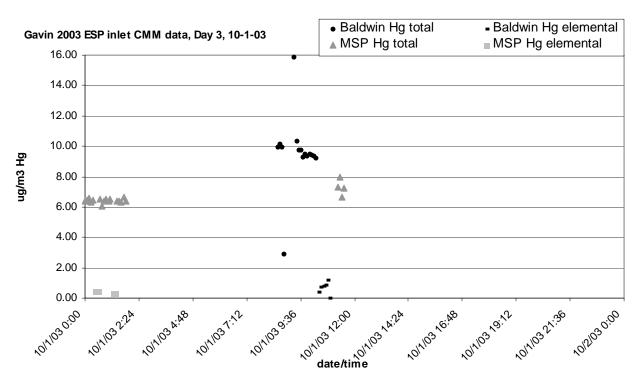


Figure 9: 10/01/03 CMM data at ESP inlet

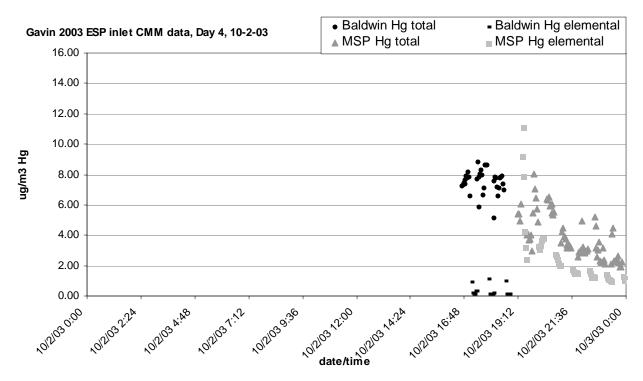


Figure 10: 10/02/03 CMM data at ESP inlet; MSP unit shows effects of particle plugging

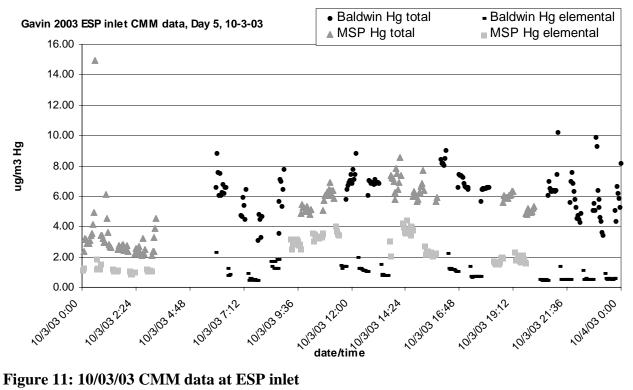


Figure 11: 10/03/03 CMM data at ESP inlet

Table 3 Daily averages for mercury in  $\mu g/m^3$  with standard deviations

Date	9/30/2003	10/1/2003	10/2/2003	10/3/2003
Baldwin Total	8.89	9.61	7.54	6.39
Baldwin Total STDEV	1.09	2.47	0.77	1.28
Baldwin Elemental	0.64	0.66	0.31	0.88
Baldwin Elemental STDEV	0.52	0.39	0.32	0.42
% elemental	7.24%	6.87%	4.06%	13.72%
MSP Total	7.56	6.61	3.88	4.78
MSP Total STDEV	2.65	0.44	1.46	1.93
MSP Elemental	0.66	0.38	2.56	2.39
MSP Elemental STDEV	0.05	0.06	2.21	0.99
% elemental	8.72%	5.73%	66.04%	49.92%

Table 4 OH values at the ESP Inlet corrected to at stack concentrations

Date/time	9/19/03 10:10	9/25/03 13:45	9/26/03 8:55	Units
Particulate	0.00	0.01	0.00	(μg/Nm³)
gas phase total	11.57	9.64	7.52	(μg/Nm³)
gas phase elemental	0.18	0.33	0.08	(μg/Nm³)

#### **Gas-Phase Mercury Results**

The MSP sampling system generally resulted in comparable total gas-phase mercury concentrations when compared to the Baldwin sampling system. However, when the MSP sampling system experienced particle plugging in one of the VI elbows that connects the VI with the cross-flow filter, a gradual decrease in the total mercury concentration was observed.

The MSP sampling system gave somewhat higher elemental gas phase mercury concentrations when compared with the Baldwin sampling system. No evident reason has been found for this behavior, so more testing needs to be done to address this issue. The change in SCR operation caused a change in mercury oxidation during the test period. The SCR was bypassed on 10/03/03. The information after shut down of the SCR could not be used as a viable comparison due to the SCR being turned back on during evenings, so steady state was not achieved. It should be noted that before 10/3/03 the elemental mercury concentrations were low and potentially within the error of measurement with the mercury analyzer.

#### **Conclusions**

- The MSP sampling system provided comparable total mercury concentrations compared to the Baldwin sampling system when operated without particle plugging taking place.
- More testing is required to obtain reliable information on the measurement of elemental mercury.
- MSP sampling system requires improvement in the following aspects:
  - o Provide large radius elbows on the back-pulsing lines.
  - o Provide a temperature controlled sampling line from the cross-flow filter to the flange on the sampling port
  - o Provide a valve that can be heat-traced on the sample line for automatic back-pulse cleaning cycles at regular intervals
  - o Reduce the internal diameter of the cross-flow filter to maintain the filter element cleaner during operation.

#### Recommendations

- The MSP sampling system should be tested again at a plant with higher amounts of oxidized and elemental mercury.
- Two conversion units and two analyzers should be used side by side to provide simultaneous comparison of the different sampling systems.
- OH values should be taken during the CEM testing for additional comparison.

# **REFERENCES**

- 1. Liu, B. Y. L., Roberts, D. L., Marple, V. A. and Romay, F. J., Sampler for Eliminating Particle-Related Artifacts for Flue Gas Measurement, United States Patent 6,561,045 B2, May 13, 2003.
- 2. Marple, V. A. and Liu, B. Y. L., *High Volume Virtual Impactor*, <u>United States Patent</u> 4,670,135, June 2, 1987.
- 3. Marple, V.A. and Chien, C. M., *Virtual Impactors: A Theoretical Study*, Environmental Science and Technology, 14:976-985, 1980.
- 4. Roberts, D. L., Romay, F. J., Laudal, D. L. and Dunham, G. E., A Virtual Impactor for Reducing Particle-Related Artifacts in the Real-Time Measurement of Mercury in Flue Gases, Proceedings of The U.S. EPA-DOE-EPRI Combined Power Plant Symposium and The A&WMA Specialty Conference on Mercury Emissions: Fate, Effects and Control, pp 182-211, August 20-23, 2001, Chicago, IL.
- 5. Romay, F. J., Roberts, D. L., Marple, V. A., Liu, B. Y. H. and Olson, B. A., *A High-Performance Aerosol Concentrator for Biological Agent Detection*, Aerosol Sci. and Tech, 36:217-226, 2002.